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### FINAL REPORT ON THE

WORKSHOP ON THE INTERACTION OF LASER RADIATION WITH SURFACES

FOR APPLICATION TO MICROELECTRONICS

May 4-5, 1981

Massachusetts Institute of Technology

Cambridge, Massachusetts



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# FINAL REPORT ON THE WORKSHOP ON THE INTERACTION OF LASER RADIATION WITH SURFACES FOR APPLICATION TO MICROELECTRONICS MAY 4-5, 1981 MASSACHUSETTS INSTITUTE OF TECHNOLOGY CAMBRIDGE, MASSACHUSETTS

### Abstract

A workshop was held which was devoted to the physics and chemistry of new optical processing and analysis techniques on surfaces for materials and structures of interest in microelectronics. It contained tutorial papers on topics of general interest to this technical area and reviewed progress in ongoing research. In addition, selected short talks describing recent results were presented. The workshop included talks from various groups throughout the United States and Europe. Attendance numbered 87.

### Introduction

Within the last two years, there have been important advances in developing new processing techniques for microelectronics which are based, in general, on photochemical and thermochemical processes initiated at a gas-solid or liquid-solid interface, by a focused laser beam. In addition, several novel optical techniques including stimulated Raman scattering are being developed for analysis of surface conditions of solid-interfaces.

The remarkable progress and interest in developing these techniques made it appropriate to hold a topical workshop devoted to the physics and chemistry of new optical processing and analysis techniques on for microelectronics.

The Organizing Committee decided to hold the conference at the Massachusetts

Institute of Technology after Professor Paul Penfield of the M.I.T. Department of Electrical Engineering and Computer Science Department graciously offered to support the workshop with the facilities of the M.I.T. VLSI effort. In addition, M.I.T. provided a convenient and accessible location for much of the U.S. microelectronics and academic communitative of TRANSMITTAL TO DTIC

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MATTHEW J. KERPER

Chief, Technical Information Division

The Committee decided also that the Workshop would contain tutorial papers on topics which were of general interest to this technical area or which would review progress in relevant ongoing research. In addition, selected talks describing pertinent recent results would be presented. Since laser annealing and conventional UV photolithography had been covered adequately in other conferences, they were not be discussed here.

### Conference Committee

The Conference Committee was selected to provide representatives of the various disciplines which made up the content of the workshop. In addition, care was taken to provide a geographically diverse viewpoint.

### Committee members were:

- R. M. Osgood (M.I.T. L.L.) Chairman
- H. Schlossberg (AFOSR Physics)
- H. I. Smith (M.I.T. Microfabrication)
- J. Yardley (Allied Corp. Laser Chemistry)
- G. Wright (ONR Solid State Physics)
- L. R. Reif (M.I.T. Processing for Microelectronics)
- J. Plummer (Stanford Solid State Chemistry)
- B. B. Lory ( M.I.T. Local Arrangements)

### Attendance

Because of the breadth of subject matter, the workshop was interdisciplinary. The workshop included contributions from academic, government, and industrial professionals in the fields of surface chemistry, solid-state physics and devices, processing science, optical physics and chemistry, microfabrication, and chemical kinetics.

Attachment 1 provides the names and affiliations of the workshop attendees.



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### Summary of Workshop

On May 4 and 5, a collection of scientists from throughout the U.S. and Europe met to discuss the impact of a new form of laser processing on micro-electronics technology. This workshop was held at Massachusetts Institute of Technology in conjunction with the Department of Electrical Engineering and Computer Science. It was sponsored by the Air Force's Office of Scientific Research (AFOSR). The meeting highlighted the new microelectronic processing options which laser-enhanced surfaces chemistry can provide, and it indicated the many potential, near-term applications of this laser processing. In addition, the importance of precise laser spectroscopy in diagnosing many forms of semiconductor processing was stressed. Tutorial talks on conventional processing techniques provided the necessary perspective for judging the emerging laser technology.

Approximately ninety scientists from universities and from government and industrial laboratories attended. The meeting was interdisciplinary in scope, including such topics as processing applications, chemical kinetics, surface science, laser spectroscopy, and solid-state physics.

The meeting, which was organized by Richard Osgood of M.I.T. Lincoln Laboratory, was opened with a technical charge by Paul Penfield, Jr. of M.I.T. for laser researchers to provide optical-based solutions to many problems facing VLSI technology. Dr. Howard Schlossberg, of AFOSR, forcefully expressed the DoD's interest in expanding the role of lasers to create new forms of electronic devices and device processing.

The bulk of the meeting was devoted to examining the important new advances in semiconductor processing which are based on laser-initiated interface chemistry. A group from M.I.T. Lincoln Laboratory described the use of laser photochemical processes to dope, etch, and deposit on semiconductors. These techniques are being applied to various problems in processing of VLSI

circuits and ultrafast microelectronic components. A group from Livermore
National Laboratory, headed by Lowell Wood, described the potential
application of these "direct-write" laser techniques to near-term, real time
design of a new generation of computers. Laverne Schlie, of the USAF Weapons
Laboratory, described the use of laser photodeposition to produce defect-free
thin-films for high-power laser mirrors.

A talk on the application of lasers to ultrasmall-area eletrochemical plating was presented by Robert J. Von Gutfeld from IBM. This process potentially eliminates excessive use of gold on electrical contacts for IC's. Presentations on other techniques for laser deposition described the use of transition-metal salts (Robert Karlicek and V. Donnelly, Bell Labs) and solid meltallo-polymers (Vernon Porter, Texas Instruments, Inc.). Deposition via thermally-driven laser CVD is also being investigated by a group at Xerox with the end goal of producing linear conductors for large area flat-panel displays.

Laser etching resulting from infrared-laser multiphoton dissociation is also being studied for use as a selective dry etching process for silicon processing. Two groups, headed by Chuang of IBM, and Jeffrey I. Steinfeld of M.I.T., respectively, are active in this area.

### Note on Organization of Workshop

The organizers of this workshop relied heavily on a computer system located in M.I.T.'s Research Laboratory of Electronics (RLE). Its textediting program was used for nearly all written text concerning the workshop, including the original proposal, the pages of abstracts distributed to each attendee, and this final report. Its address management system recorded invitees, registrants, registration payments, address corrections and changes, and printed the registration list distributed at the workshop and the name badges.

### Final Workshop Program

Attachment 2 contains the final agenda and the abstracts of each talk. In addition, there was one poster talk, "Theoretical Study of Laser-Simulated Surface Processes Involved in Chemical Vapor Deposition," by T. F. George, A. C. Beri, J. Lin, and W. C. Murphy, University of Rochester. That abstract is the final page of Attachment 2.

### Attendance List

## Workshop on the Interaction of Laser Radiation with Surfaces

### for Application to Microelectronics

May 4-5, 1981

Dimitri A. Antoniadis Room 13-3014 Mass. Inst. of Tech. Cambridge, MA 02139

J. Berg R1\1196 TRW One Space Park Redondo Beach, CA 90278

Avinash C. Beri Department of Chemistry University of Rochester Rochester, NY 14627

Jerry G. Black Xerox Corporation Xerox Square-114 Rochester, NY 14644

Claudia Borman Harvard University Cambridge, MA 02138

Kirk Boyer Rm. B212, ERC Research Ctr. Colorado State University Fort Collins, CO 80523

W. G. Breiland
Division 4216
Sandia Laboratories
KAFB, P. O. Box 5800
Albuquerque, NM 87185

Walter Brown Room 1E452 Bell Laboratories 600 Mountain Ave. Murray Hill, NJ 07974 Steven R. J. Brueck Room C-172 M.I.T. Lincoln Laboratory P. O. Box 73 Lexington, MA 02173

Gary Carter GTE Laboratories 40 Sylvan Road Waltham, MA 02254

George K. Celler Bell Laboratories 600 Mountain Ave. Murray Hill, NJ 07974

Yung-Jui Chen Advanced Technical Lab GTE Laboratories 40 Sylvan Road Waltham, MA 02254

Jeffrey T. Cheung Rockwell International 1049 Camino Dos Rios Thousand Oaks, CA 91360

Tung J. Chuang K33-281 IBM Research Laboratory 5600 Cottle Rd. San Jose, CA 95193

Charles Clahasy Room C-166 M.I.T. Lincoln Laboratory P. O. Box 73 Lexington, MA 02173 John W. Coburn K33\281 IBM Research Laboratory 5600 Cottle Rd. San Jose, CA 95193

George Collins
Dept. of Electrical Eng.
Colorado State University
Fort Collins, CO 80523

Robert D. Coombe Science Center Rockwell International 1049 Camino Dos Rios Thousand Oaks, CA 91360

Stephen M. Copley Dept. of Materials Science Univ. of Southern California University Park Los Angeles, CA 90007

Vincenzo Daneu M.I.T. Lincoln Laboratory P. O. Box 73 Lexington, MA 02173

C. David Decker GTE Laboratories 40 Sylvan Road Waltham, MA 02254

Thomas F. Deutsch Room C-128 M.I.T. Lincoln Laboratory P. O. Box 73 Lexington, MA 02173

Gene Dresselhaus Room NW14-4117 Mass. Inst. of Tech. Cambridge, MA 02139 Charles Duke
W114
Xerox Corporation
Xerox Square-114
Rochester, NY 14644

Nicholas Economou Room I-300 M.I.T. Lincoln Laboratory P. O. Box 73 Lexington, MA 02173

J. G. Eden
Dept. of Electrical Eng.
University of Illinois
Urbana, IL 61801

Daniel Ehrlich Room C-177 M.I.T. Lincoln Laboratory P. O. Box 73 Lexington, MA 02173

R. B. Fair Room 30-171 Bell Laboratories 2525 N. 11th Street Reading, PA 19604

John Flint Room 3-235 Mass. Inst. of Tech. Cambridge, MA 02139

George Flynn
315 Havemeyer Hall\Chemistry
Columbia University
New York, NY 10027

Michael Geis Room I-300 M.I.T. Lincoln Laboratory P. O. Box 73 Lexington, MA 02173

H. P. Gillis Hughes Research Laboratory 3011 Malibou Canyon Rd. Malibou, CA 90265

Joe Greene
Department of Metallurgy
University of Illinois
Urbana, IL 61801

John Haggerty Room 12-011 Mass. Inst. of Tech. Cambridge, MA 02139

D. Harradine Room 2-013, Chemistry Mass. Inst. of Tech. Cambridge, MA 02139

Irving P. Herman L-372 Lawrence Livermore Nat. Lab. P.O. Box 808 Livermore, CA 94550

R. T. Hodgson IBM T. J. Watson Rsch. Ctr. P. O. Box 218 Yorktown Heights, NY 10598

Robert Karlicek Room 7C-314 Bell Laboratories 600 Mountain Ave. Murray Hill, NJ 07974

Eric Kay K33-028 IBM Research Laboratory 5600 Cottle Rd. San Jose, CA 95193

Paul Kelley Room C-128 M.I.T. Lincoln Laboratory P. O. Box 73 Lexington, MA 02173

C. S. Kim Digital Equipment Corp. 75 Reed Road Hudson, MA 01749

Henri Lezec Mass. Inst. of Tech. 400 Memorial Drive Cambridge, MA 02139

Paul Liao Bell Laboratories Holmdel, NJ 07733

Jui-teng Lin Department of Chemistry University of Rochester Rochester, NY 14627 Edward Maby Room 13-3018 Mass. Inst. of Tech. Cambridge, MA 02139

Raymond Mariella Corporate Headquarters Allied Chemical Corp., MRC P.O. Box 1021R Morristown, NJ 07960

Robert Marra Room 12-096 Mass. Inst. of Tech. Cambridge, MA 02139

Jere M. Marrs MS 50-324 Tektronix, Inc. P.O. Box 500 Beaverton, OR 97077

F. Read McFeely Room 6-133 Mass. Inst. of Tech. Cambridge, MA 02139

William McNeil GTE Laboratories 40 Sylvan Road Waltham, MA 02254

Rajendra S. Mehta HL1-1\R10 Digital Equipment Corp. 75 Reed Road Hudson, MA 01749

G. L. Olson Hughes Research Laboratory 3011 Malibou Canyon Rd. Malibou, CA 90265

Richard Osgood Room C-166 M.I.T. Lincoln Laboratory P. O. Box 73 Lexington, MA 02173

Michael Paesler Physics Dept. No. Carolina State Univ. Raleigh, NC 27612

Paul Penfield, Jr. Room 36-575 Mass. Inst. of Tech. Cambridge, MA 02139 Vern Porter
Mail Stop 118
Texas Instruments
P. O. Box 225936
Dallas, TX 75265

Maurice Pyee Laboratoire RMN Universite PM Curie Paris VI 4 Place Jussieu Paris, France 75005

Victor Rehn Michelson Lab-3813 NWC China Lake, CA 93555

Rafael Reif Room 13-3082 Mass. Inst. of Tech. Cambridge, MA 02139

Bobbi Roop Room 2-121, Chemistry Mass. Inst. of Tech. Cambridge, MA 02139

Sven Roosild DARPA 1400 Wilson Blvd. Arlington, VA 22209

Shlomo Rotter Room 13-3070 Mass. Inst. of Tech. Cambridge, MA 02139

Rene Salathe
Inst. of Applied Physics
University of Berne
Silderstrasse 5
CH-3012 Bern, Switzerland

Herbert Sawin Room 66-464 Mass. Inst. of Tech. Cambridge, MA 02139

L. A. Schlie Air Force Weapons Lab KAFB Albuquerque, NM 87117

Howard Schlossberg AFOSR 4811 Hercules Court Annandale, VA 22003 F. Schreiner
Department of Chemistry
North Carolina State Univ.
Raleigh, NC 27650

Charles V. Shank Bell Laboratories Holmdel, NJ 07733

Donald Silversmith Room E-118K M.I.T. Lincoln Laboratory P. O. Box 73 Lexington, MA 02173

Henry I. Smith Room 13-3061 Mass. Inst. of Tech. Cambridge, MA 02139

William Spicer McGullough 228\Elec. Lab Stanford University Stanford, CA 94305

Jeffrey Steinfeld Room 2-221 Mass. Inst. of Tech. Cambridge, MA 02139

Susan Tarr
Engineering Research Center
Western Electric
P. O. Box 900
Princeton, NJ 08540

H. R. Thomas Xerox Corporation Xerox Square-114 Rochester, NY 14644

Gary Tisone Division 4212 Sandia Laboratories KAFB, P. O. Box 5800 Albuquerque, NM 87185

Nyle Utterback Bldg. R-1, 1196 TRW One Space Park Redondo Beach, CA 90278

Robert J. von Gutfeld IBM T. J. Watson Rsch. Ctr. P. O. Box 218 Yorktown Heights, NY 10598 H. Weber
Institute of Applied Physics
University of Berne
Silderstrasse 5
CH-3012 Bern, Switzerland

Andrew H. Weisberg L-372 Lawrence Livermore Nat. Lab. P.O. Box 808 Livermore, CA 94550

Jonathan White Room 4C316 Bell Laboratories Holmdel, NJ 07733

Horst R. Wittmann
U. S. Army Research
P. O. Box 12211
Research Triangle Pk NC 27709

Frank Wodarczyk Science Center Rockwell International 1049 Camino Dos Rios Thousand Oaks, CA 91360

Thomas H. Wood Room 4B-429 Bell Laboratories Holmdel, NJ 07733

George Wright
Code 427
Office of Naval Research
800 N. Quincy St.
Arlington, VA 22217

James Yardley Allied Chemical Company Box 1021 R Morristown, NJ 07960

David M. Zehner Solid State Division Oak Ridge National Lab P.O. Box X Oak Ridge, TN 37830

Herbert Zeiger C-130 M.I.T. Lincoln Laboratory P. O. Box 73 Lexington, MA 02173



DEPARTMENT OF ELECTRICAL ENGINEERING AND COMPUTER SCIENCE

# MASSACHUSETTS INSTITUTE OF TECHNOLOGY CAMBRIDGE, MASSACHUSETTS 02139

WORKSHOP ON THE INTERACTION OF LASER RADIATION
WITH SURFACES FOR APPLICATION TO MICROELECTRONICS
May 4-5, 1981
M.I.T. Stratton Student Center
Cambridge, Massachusetts

### PROGRAM

### Monday, May 4, 1981

Session I. Chai	irman: Howard Schlossberg
8:30 - 8:45	WELCOME Professor Paul Penfield, M.I.T.
8:45 - 9:05	Introductory Remarks, Dr. Howard Schlossberg, AFSOR
9:05 - 9:40	"Laser Processing of Semiconductors," W.L. Brown, Bell Laboratories, Murry Hill, NJ
9:40 - 10:1	"Limitations and Benefits of Standard High Temperature Processing in Producing Device Quality Silicon Surface Layers," R.B. Fair, Bell Laboratories, Reading, PA
10:15 - 10:3	COFFEE BREAK
10:35 - 11:1	"Ion-Enhanced Gas-Surface Chemistry," J.W. Coburn, IBM Research Laboratory, San Jose, CA
11:10 - 11:4	"Interaction of Light with Molecules on Surfaces,"  J.T. Yardley, Allied Chemical Corporation, Morristown, NJ
11:45 - 1:10	LUNCH: Informal sandwich buffet, Room 209
Session II. Chai	rman: Thomas Deutsch
1:10 - 1:45	"Laser Microchemistry for Electronics," D.J. Ehrlich, R.M. Osgood, Jr. and T.F. Deutsch, Lincoln Laboratory, M.I.T.
1:45 - 2:15	"Infrared Laser Enhanced Gas-Surface Chemistry: Chemical Etching of Metal and Semiconductor Materials," T.J. Chuang, IBM Research Laboratory, San Jose, CA
2:20 - 2:35	"Deposition of Thin Amorphous Si and Ge Films by the Ultraviolet Photodissociation of Silane or Germane," R.W. Andreatta, J.G. Eden, D.Lubben, and J.F. Greene, University of Illinois at Urbana-Champaign, Urbana, IL

Monday, May 4, 1981 (continued)  2:35 - 3:00 "Visible Light Induced Dep	position of Cd on Transparent
2:35 - 3:00 "Visible Light Induced Den	
Substrates," R.P. Salat	University of Bern, Bern
	Refractory Metals," P.K. Boyer and State University, Fort
3:25 - 3:40 COFFEE BREAK	
Salt Solutions," R. Kar	sition from Transition Metal Clicek, V.Donnelly, Bell Labora- J and G. Collins, Colorado State ns, CO
	Deposition (LACVD) of Metals," R. Kellerman and H.R. Thomas, Center, Rochester, NY
	to Selected Area Deposition," California, Los Angeles, CA Copley
the Clean GaAs (110) Su W. Petro, I. Lindau, S.	diation on Uptake of Oxygen on orface," W.E. Spicer, I. Hino, Eglash, and C.Y. Su, Stanford Stanford University, CA

Banquet at Alexander Parris Room, Faneuil Hall Marketplace, Boston

7:00 . Cocktails

7:45 Dinner

### Tuesday, May 5, 1981

Session III. Chair	man: David Ehrlich
8:30 - 8:55	"Pulsed UV Laser Doping of Semiconductors," T.F. Deutsch, D.J. Ehrlich, and R.M. Osgood, Jr., Lincoln Laboratory, M.I.T., Lexington, MA
8:55 - 9:10	"Discretionary Photoprocessing of Wafer Surfaces with Flying Laser Spots," A.H. Weisberg, R.A. Hyde, I.P. Herman, and L.L. Wood, Lawrence Livermore National Laboratory, U. of California, Livermore, CA
9:15 - 9:30	"Photodeposition of Zn/Se/ZnSe Thin Films," L.A. Schlie, L. Rose, W.E. Johnson, Air Force Weapons Laboratory, KAFB, Albuquerque, NM
9:30 - 9:45	"Laser Microdeposition from Metallo-Polymers," V.R. Porter, Central Research Laboratories, Texas Instruments, Inc. Dallas TX
9:50 - 10:15	"Surface Properties of Laser Annealed Semiconductors," D.M. Zehner and C.W. White, Oak Ridge National Laboratory, Oak Ridge, TN
10:15 - 10:40	COFFEE BREAK
10:40 - 11:05	"Laser Enhanced Plating and Etching: Theory and Applications," R.J. von Gutfeld, R.E. Acosta and L.T. Romankiw, IBM Research Center, Yorktown Heights, NY
11:05 - 11:20	"Laser Induced Deposition of Thin Films," F.J. Wodarczyk and R.D. Coombe, Rockwell International Science Center, Thousand Oaks, CA
11:25 - 11:40	"Enhancement of ZnS Thin Film Growth by Argon-Laser Light," V. Daneu, Istituto di Elettrotecnica, Viale delle Scienze, Palermo, Italy
11:40 - 12:00	"Reactive Etching of Semiconductor Surfaces by Laser- Generated Free Radicals," D. Harradine, F.R. McFeely, B. Roop, and J.I. Steinfeld, Department of Chemistry, M.I.T. Cambridge, MA and D. Denison, L. Hartsough, and J. Hollahan, Perkin-Elmer Corporation, Mountain View, CA
12:00 - 12:20	"Ellipsometric Study of Beam-Surface Interactions," R.P. Mariella, Jr., Allied Chemical Corporation, Morristown, NJ
12:20 - 1:40	LUNCH: Mezzanine Lounge, Room 309

### Tuesday, May 5, 1981 (continued)

Session	TV.	Chairman,	Centre	Wright
DESSION	TA.	CHATTHAII,	George	MITZHIC

1:40 - 2:15	"Review of Conventional Submicron Fabrication Techniques," H.I.Smith Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA
2:15 - 2:40	"Dectection of Surface Monolayers with the Surface Enhanced Raman Effect," C.V. Shank and T. Wood, Bell Laboratories Holmdel, NJ .
2:45 - 3:05	"Studies of the Gas Phase in Chemical Vapor Deposition: Pulsed UV Raman Diagnostics and Theoretical Modelling of Silicon Deposition," W.G. Breiland, and M.E. Coltrin Sandia Labs, Albuquerque, NM
3:05 - 3:20	"Studied of Enhanced Raman Scattering with Ag Structures Produced by Microlithography," R.F. Liao, Bell Labora- tories, Holmdel, NJ
3:25 - 3:45	COFFEE BREAK
3:45 - 4:15	"DARPA Programs in Electronic Materials, Fabrication Processes and Devices," S.A. Roosild, DARPA/DSO
4:15 - 4:35	"Molecular Beam Etching of Semiconductor Surfaces," H.P. Gillis and F.G. Yamagishi, Hughes Research Laboratories, Malibou, CA "Optical Characterization of Molecular Beam Etching," G.L. Olson, H.P. Gillis, and L.D. Hess, Hughes Research Laboratories, Malibou, CA
4:35 - 4:55	"Metal Deposition Using Ultraviolet Photolysis," J. Berg and P. Yeung, TRW, Redondo Beach, CA and S. Allen, U. Southern California, Los Angeles, CA "Amorphization at Low Fluence with Laser Blow-Off Ion Source," N.G. Utterback and S. Prussin, TRW, Redondo Beach, CA
4:55 - 5:15	"Integrated Circuit Applications of Laser Deposition and Annealing of Insulator Films," J.M. Marrs, Applied Research Group, Tektronix, Inc., Beaverton, OR



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### PURPOSE OF WORKSHOP

This workshop is devoted to the physics and chemistry of new optical processing and analysis techniques on surfaces for materials and structures of interest in microelectronics. It contains tutorial papers on topics of general interest to this technical area and reviews progress in ongoing research. In addition, selected short talks describing recent results are being presented. Since laser annealing and conventional UV photolithography are covered adequately in other conferences, they are not discussed here.

### SUBJECT OF THE WORKSHOP

Within the last two years, there have been important advances in developing new processing techniques for microelectronics which are based on laser surface interaction. These techniques are based in general on photochemical and thermochemical processes initiated at a gas-solid or liquid-solid interface, by a focused laser beam. In addition, several novel optical techniques including stimulated Raman scattering are being developed for analysis of surface conditions of solid-interfaces.

This workshop includes talks, from various groups throughout the United States and Europe, which present and review these techniques and the interfacial photochemistry and surface physics necessary to understand them.

### CONFERENCE COMMITTEE

- R. M. Osgood (M.I.T.-L.L.) Chairman
- H. Schlossberg (AFOSR)
- H. I. Smith (M.I.T.)
- J. Yardley (Allied Corp.)
- G. Wright (ONR)
- L. R. Reif (M.I.T.)
- J. Plummer (Stanford)
- B. B. Lory (M.I.T.) Local Arrangements

WORKSHOP ON THE INTERACTION OF LASER RADIATION WITH SURFACES FOR APPLICATION TO MICROELECTRONICS

### **ABSTRACTS**

Monday, May 4, 1981

9:05

### Laser Processing of Semiconductors

W. L. Brown
Bell Laboratories
600 Mountain Ave.
Murray Hill, NJ 07974

The interaction of CW and nanosecond pulsed lasers with semiconductors provides new opportunities for rapid and localized thermal processing. Some of the most interesting possibilities arise when the near surface temperature exceeds the melting point: rapid epitaxial crystallization occurs on crystalline substrates and crystal growth occurs on amorphous substrates as well. The science and application of these phenomena will be discussed.

9:40

# Limitations and Benefits of Standard High Temperature Processing in Producing Device Quality Silicon Surface Layers

R. B. Fair Bell Laboratories Reading, PA

Thermal diffusion of doping impurities and silicon exidation are two of the most important processes in the microelectronic fabrication arsenal. However, these processes can upset the dynamic balance in silicon between dissolved impurities, point defects, surface bonding arrangements, and microdefects to yield degraded devices. On the other hand, these processes can also yield device quality silicon layers if their benefits and limitations are understood. This talk deals with the fundamentals of these benefits and limitations.

10:35

### Ion-Enhanced Gas-Surface Chemistry

John W. Coburn IBM Research Laboratory San Jose, CA 95193

Ion-enhanced gas-surface chemistry is believed to be responsible for the etching directionality which can be obtained in most plasma etching systems. This talk will review some surface-science oriented studies of this phenomenon carried out with ion beams and fluxes of chemically active neutral gaseous species in a high vacuum environment using the silicon-fluorine system as an example.

### Interaction of Light with Molecules on Surfaces

James T. Yardley Allied Chemical Corp. Morristown, NJ 07960

Light can interact with individual molecules on surfaces either directly through vibrational or electronic excitation, or indirectly through thermal heating of the substrate. These interactions may be used to carry out specific chemical and physical transformations. Some general means for carrying out such transformations will be described, along with a few selected examples.

1:10

### Laser Microchemistry for Electronics\*

D. J. Ehrlich, R. M. Osgood Jr. and T. F. Deutsch M.I.T. Lincoln Laboratory Lexington, MA 02173

A laser beam can be used to activate a reaction at a gas/solid interface by photochemical or thermal excitation of gas-phase or adsorbed molecules. The same beam can simultaneously confine the reaction to micrometer dimensions on the surface via a number of physical processes including control of reaction rates, initiation of product nucleation, or by adsorption or desorption of surface catalysts or contaminants. In this paper we show that the high spatial control associated with laser stimulation of surface chemistry can be the basis of a new class of direct, maskless, fabrication techniques for microelectronics.

\*This work was supported by the Department of the Air Force, in part under a specific program sponsored by the Air Force Office of Scientific Research, by the Defense Advanced Research Projects Agency and by the Army Research Office.

1:45

# Infrared Laser Enhanced Gas-Surface Chemistry: Chemical Etching of Metal and Semiconductor Materials

T. J. Chuang
IBM Research Laboratory
5600 Cottle Road, San Jose, CA 95193

Infrared laser induced interactions of  $SF_6$  and  $XeF_2$  gases with Si,  $SiO_2$ . Ta and Te surfaces have been studied and the surface reaction yields have been determined as a function of the laser wavelength, the laser intensity and the gas pressure in both perpendicular and parallel beam incidences on the solids. Various laser-enhanced reaction mechanisms have been identified from XPS and mass spectrometric analyses. Aspects of laser-induced chemical etching will be discussed.

# Deposition of Thin Amorphous Si and Ge Films by the Ultraviolet Photodissociation of Silane or Germane\*

R. W. Andreatta and J. G. Eden Electrical Engineering Department

D. Lubben and J. E. Greene
Department of Metallurgy
Coordinated Science Laboratory
University of Illinois at Urbana-Champaign
Urbana. IL 61801

The rapid deposition of a-Si and a-Ge films on various substrates at room temperature has been obtained by photodissociating silane (or SiCl $_{\parallel}$  or (CH $_{3}$ ) $_{\parallel}$ Si) and germane, respectively, with the ultraviolet output of a pulsed ArF (193 nm) or KrF (248 nm) excimer laser. Deposition rates of 80-90 Å-s-1 have been observed and the resulting films exhibit large sheet resistivities (> 10 $^{7}$   $\Omega/\Box$ ) and excellent adhesion properties.

\*This work is supported in part by the Joint Services Electronics Program.

2:35

### Visible Light Induced Deposition of Cd on Transparent Substrates

R. P. Salathé, Y. Rytz-Froidevaux, H. H. Gilgen, and H. P. Weber Institute of Applied Physics University of Berne CH-3012 Bern, Switzerland

Laser initiated deposition mechanisms of Cd from dimethylcadmium (DMCD) on quartz substrates have been investigated at various wavelengths between 337 and 676 nm. In this range substrate and DMCD are transparent. The nonlinear formation process is explained by multiphoton dissociation and pyrolysis which starts after initial formation of an embryos film.

3:05

### Laser Photodeposition of Refractory Metals\*

P. K. Boyer and G. J. Collins
Department of Electrical Engineering
Colorado State University
Fort Collins, CO 80523

Room temperature deposition of Cr. Mo and W by photodissociation of their respective hexacarbonyls has been demonstrated on various insulators and semiconductors. We compare depositions made with a 192 nm ArF laser and a 260 nm Cu II laser, with economical, single step patterned metal deposition as a goal. Patterned growth and deposition of insulators is also under investigation.

<sup>\*</sup>This work is supported by the National Science Foundation and the Office of Naval Research.

# Laser Induced Metal Deposition from Transition Metal Salt Solutions

R. Karlicek and V. Donnelly Bell Laboratories, Murray Hill, NJ 07974

G. J. Collins

Department of Electrical Engineering

Colorado State University

Fort Collins, CO 80523

It has been demonstrated that platinum can be deposited on p-type, n-type, and undoped InP via pulsed laser irradiation of polished InP substrated immersed in an aqueous solution of chloroplatinic acid. Pulsed laser intensities sufficient to initiate thermal decomposition of the InP surface, yet below the threshold at which gross surface damage occurs, cause elemental platinum to be deposited on the InP surface. The platinum deposits in the form of rectangular islands on the  $\langle 100 \rangle$  InP surface and trigonal structures on the  $\langle 111 \rangle$  InP surface. Under certain conditions, the islands grow together to form smooth platinum films 0.5  $\mu$ m thick. Auger electron analysis indicates that the platinum deposits are free of oxygen and chlorine contamination. Preliminary results also indicate that this technique may be used to deposit platinum on GaAs, nickel on InP (using aqueous NiSO $_{ij}$  solutions) and gold on InP (using aqueous HAuCl $_{ij}$  solutions). Platinum and gold deposits on InP exhibit ohmic behavior.

4:05

### Laser Assisted Chemical Deposition (LACVD) of Metals

J. G. Black, C. B. Duke, R. Kellerman, and H. R. Thomas Xerox Webster Research Center Rochester, NY 14644

The Xerox Webster Research Center supports a small exploratory effort on the LACVD of metals. The objectives of this effort are to define the latitudes of the deposition process and to prepare high-quality films of reactive metals, especially aluminum. In this presentation the context of the program, the present process model, and the current status of the experimental implementation of the LACVD process and the characterization of the resulting materials will be indicated.

4:40

### Laser CVD - Applications to Selected Area Deposition\*

Susan D. Allen
Center for Laser Studies
University of Southern California
Los Angeles, CA 90007

Laser chemical vapor deposition (LCVD) has been used to deposit films of metals and dielectrics on several different substrates with both pulsed and cw laser sources. Characteristics of the LCVD films such as thickness, deposition rate, spatial resolution, resistivity, and physical properties will be discussed as a function of irradiation conditions.

<sup>\*</sup>This work is supported in part by a grant from AFOSR under the technical direction of H. Schlossberg.

# Effect of Mild Laser Irradiation on Uptake of Oxygen on the Clean GaAs(110) Surface\*

William E. Spicer, Isao Hino, W. Petro, I. Lindau, S. Eglash, and C. Y. Su Stanford Electronics Laboratory Stanford University, Stanford, CA

Because of the debate as to whether laser annealing is or is not a purely thermal effect, and because of the importance of the oxygen surface chemistry on 3-5 semiconductors, we have studied the effect of mild laser irradiation on the oxidation behavior of (110) faces of GaAs cleaved in UHV (10-10 torr). The oxygen sticking probability in the submonolayer coverage range has been increased by a factor of 103 (from a probability of approximately  $10^{-9}$  to  $10^{-6}$ ) by uniform irradiation with an argon (5145 Å) CW laser at approximately 0.5 watt/cm2 on the GaAs surface. However, the binding of the oxygen so formed is the same as that obtained by exposure to molecular oxygen in the ground state, but different from that obtained by exposure to oxygen excited by an ion gauge. To date, we find it impossible to explain our data in terms of either heating of the surface or excitation of the oxygen by the laser radiation; it appears the most likely explanation for the phenomena is an increase of the density of electrons and/or holes at the surface (the surface recombination velocity is larger in GaAs). A limiting Step in the oxygen uptake process is the break up of the oxygen molecule; this dissociation would be increased by the presence of electrons.

<sup>\*</sup>Work supported by ARPA and ONR.

### Tuesday, May 5, 1981

8:30

### Pulsed UV Laser Doping of Semiconductors

Thomas F. Deutsch M.I.T. Lincoln Laboratory Lexington, MA 02173

Doping of elemental and compound semiconductors using pulsed UV excimer lasers has been demonstrated. Both photochemical and pyrolytic dissociation of molecular gases can be used to supply doping atoms which are incorporated into a laser heated substrate. The technique has been used to make efficient Si solar cells and is being applied to GaAs technology.

8:55

# Discretionary Photoprocessing of Wafer Surfaces with Flying Laser Spots\*

Andrew H. Weisberg,\*\* Roderick A. Hyde, Irving P. Herman and Lowell L. Wood
University of California
Lawrence Livermore National Laboratory
Livermore, CA 94550

A system for executing micrometer-scale discretionary processing of semiconductor wafer surfaces is discussed. Error budgets and spot rates for such micro-fabrication via high-speed computer-controlled ultraviolet laser spot positioning and intensity modulation in vacuum and reactive atmospheres are quantified, and problems faced in the design of the required apparatus and specification of its components are noted.

9:15

### Photodeposition of Zn/Se/ZnSe Thin Films

L. A. Schlie, L. Rose, and W. E. Johnson Air force Weapons Laboratory, KAFB Albuquerque, NM 87117

Thin films of Zn. Se. ZnSe have been deposited on various substrates by the photodissociation of the organo-metallic molecules zinc and selenium dimethyl. Large thicknesses (approximately 6000 Å) and areas with 2 cm cross diameters have been produced. This technique may provide drastically improved thin films for high energy laser mirrors with much higher quality and purity. A potential two-step process will also be discussed.

<sup>\*</sup>Work performed under the auspices of the U. S. Department of Energy under Contract W-7405-Eng-48.

<sup>\*\*</sup>Fannie and John Hertz Foundation Fellow, Stanford University.

### Laser Microdeposition from Metallo-Polymers

Vernon R. Porter
Central Research Laboratories
Texas Instruments Incorporated
Dallas, TX 75265

Metals and crosslinked metal polymers have been selectively deposited on glass and metal substrates. A focused cw-argon laser was used in both multicolor and at the 5145 Å line. Deposits of gold, rhodium, molypdenum and copper were deposited in spots typically from 50 micron to 5 micron diameter and 1000 Å-5000 Å thick. The polymer carrier exhibits a strong influence on the adherence and topography of the deposit obtained.

9:50

### Surface Properties of Laser Annealed Semiconductors\*

D. \*\*. Zehrer and C. W. White Solid State Division
Oak \*\*.dge National Laboratory
Oak Ridge, TN 37830

The surface regions of single crystal semiconductors have been examined following laser irradiation in an ultra-high vacuum environment with the output of a pulsed ruby laser. Atomic, geometric and electronic properties have been determined by using AES, LEED and PES techniques. The production of clean, ordered and metastable surfaces along with comparisons with results obtained by conventional preparation techniques will be discussed.

\*Research sponsored by the Division of Materials Science, U.S. Department of Energy, under contract W-7405-eng-26 with Union Carbide Corporation.

10:40

### Laser Enhanced Plating and Etcning: Theory and Applications

R. J. von Gutfeld, R. E. Acosta and L. T. Romankiw IBM T. J. Watson Research Center Yorktown Heights, NY 10598

We have observed local enhancement factors on the order of  $103-10^4$  for electroplating (electroetching) rates by irradiating the cathode (anode) by a focused laser beam. Enhanced electroless and exchange plating rates have also been observed. A thermal model is used to explain all of the observed results. Some applications, particularly to the repair of microelectronic circuits, will be discussed.

### Laser Induced Deposition of Thin Films\*

F. J. Wodarczyk and R. D. Coombe Rockwell International Science Center Thousand Oaks, CA 91360

Within the last year, experiments at the Rockwell International Science Center have investigated two laser-based thin film deposition methods. In the first technique, lasers have been used to desorb surface materials which inhibit normal adhesion of the species to be deposited, or which otherwise prevent surface processing. The second method involves the use of lasers to drive chemical reactions which produce the desired film on the substrate surface. Both methods offer the possibility of vast simplification in the production of localized films as well as improvements in their physical and mechanical properties.

\*Research supported by Rockwell International Independent Research and Development funds.

11:25

### Enhancement of ZnS Thin Film Growth by Argon-Laser Light

V. Daneu\*
Istituto di Elettrotecnica
Viale delle Scienze
Palermo, Italy

The growth of a ZnS layer on a CdS-coated substrate is found to be strongly influenced by illumination with 4880 Å light of relatively low intensity (.1 to 1W/cm²). The effect is critically dependent on the surface conditions at the CdS-ZnS interface and shows a spatial resolution extending at least into the micron range. A sensitive technique for real time mapping of the light-induced film growth has been developed.

<sup>\*</sup>Currently on leave at M.I.T. Lincoln Laboratory, Lexington, MA.

# Reactive Etching of Semiconductor Surfaces by Laser-Generated Free Radicals\*

David Harradine, F. Read McFeely, Bobbi Roop, and Jeffrey I. Steinfeld
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139

Dean Denison, Larry Hartsough, and John Hollahan Plasma Products Division, Perkin-Elmer Corporation Mountain View, CA 94043

Reactive etching at silicon and silicon-oxide surfaces is customarily carried out in a fluorocarbon plasma. Under such conditions, a large variety of reactive species is generated, making it extremely difficult to elucidate details of the etching mechanism; in addition, the charged species present in the plasma frequently produce undesirable radiation damage in the finished devices. We have found that dissociation of the parent fluorocarbons by multiple-infrared-photon excitation produces reactive neutral fragments which are capable of etching these surfaces. Experiments with Cf<sub>3</sub>Br; Cf<sub>2</sub>HCl; CF<sub>3</sub>OOCF<sub>3</sub>, SF<sub>6</sub>, and other etch gases will be described; SEM, ESCA, and Auger diagnostics are employed to characterize the reactions occurring at the surface. From these experiments we hope to develop a quantitative model for the reactive etching process. Possible commercial advantages of the laser-etching technique include reduction or elimination of radiation damage, increased etching rates, and improved SiO<sub>2</sub>/Si specificity.

\*Supported by National Science Foundation Industry-University Cooperative Research Program Grant No. CHE 79-26248.

12:00

### Ellipsometric Study of Beam-Surface Interactions

R. P. Mariella Jr.
Allied Chemical Corporation
Morristown, NJ 07960

Spectroscopic ellipsometry has been used to measure the effective complex dielectric constants for CdS surfaces as a function of surface preparation, temperature, and film thickness.

1:40

### Review of Conventional Submicron Fabrication Techniques

Henry I. Smith

Department of Electrical Engineering and Computer Science Massachusetts Institute of Technology, Cambridge, MA 02139

This conference is concerned primarily with the use of lasers in the fabrication of thin film microstructures. Such laser-based techniques complement a rather broad range of microfabrication techniques based on the exposure of a "resist" film with a pattern of electron, ion or photon radiation, followed by processes of etching, doping, growth or deposition. The essential features and limitations of these "conventional" techniques will be reviewed briefly with emphases on methods compatible with linewidths in the range  $1\,\mu$ m to 1 nm.

### Detection of Surface Monolayers with the Surface Enhanced Raman Effect

C. V. Shank and T. Wood Bell Laboratories Holmdel, NJ 07733

Recent adventures in light scattering techniques applicable to detecting sub-monolayer adsorbate coverages on metals will be discussed.

2:45

Studies of the Gas Phase in Chemical Vapor Deposition: Pulsed UV Raman Diagnostics and Theoretical Modelling of Silicon Deposition\*

W. G. Breiland and H. E. Coltrin Sandia Laboratories Albuquerque, NM 87185

When the contraction of the cole that Jas-phase chanical kinetics plays in the CVD process.

Pulsed UV Raman spectroscopy has been successfully employed to measure gas-phase silane density profiles inside a horizontal flow CVD reactor. Hydrogen gas as a product of silane pyrolysis has also been detected. Preliminary studies have shown that pulsed UV Raman spectroscopy can be successfully employed as a diagnostic tool for many CVD reactions of interest to the microelectronics industry.

To complement these experiments, a computer model has been developed for the coupled gas-phase kinetics and hydrodynamics in a horizontal-flow CVD reactor. The code predicts flow streamlines, profiles of temperature, velocity and chemical species concentrations, and deposition rates as functions of susceptor temperature, reactant and carrier gas pressures and flow velocity.

\*This work supported by the U. S. Department of Energy.

3:05

# Studies of Enhanced Raman Scattering wtn Ag Structures Produced by Microlithography

P. F. Liao Bell Laboratories Holadel. NJ 07733

Modern techniques of microlithography are used to produce microstructure silver particle arrays. The particles have approximately 1000% dimensions and are obtained by evaporation of silver onto a microstructure composed of 1000% diameter SiO<sub>2</sub> posts on a silicon substrate. These arrays elucidate the mechanism of enhanced Raman scattering.

# DARPA Programs in Electronic Materials, Fabrication Processes and Devices

Sven A. Roosild
DARPA/DSO
Arlington, VA 22209

DARPA research programs in electronic materials, processes, and device structures explore fundamental physical phenomena, new materials systems, fabrication techniques, and novel device concepts which, if reduced to practice, would provide significant new technological options to implement future DOD electronic systems concepts. The program emphasizes pursuit of novel, high risk-high payoff approaches derived from efforts into the fundamental understanding of physical phenomena in solid-state electronics. The present emphasis is in four technological areas: VLSI research, high throughput circuits, infrared focal plane arrays, and advanced electronic materials.

4:15

### Molecular Beam Etching of Samiconductor Surfaces

H. P. Gillis and F. G. Yamagishi Hughes Research Laboratories Malibou, CA 90265

The technique of molecular beam stening (MOSE), under development at HRL, shows promise for profile control in fabrication of submicroaster features. Because the chemistry in the beam environment is simpler and better controlled than in conventional plasma reactors, laser optical and spectroscopic techniques are immediately applicable to monitoring of rates and products. These techniques should be especially useful in elucidation of the etcning mechanism.

### Optical Characterization of Molecular Beam Etching

G. L. Olson, H. P. Gillis, and L. D. Hess Hughes Research Laboratories Malibou, CA 90265

Optical techniques for probing the kinetics and for determining the mechanisms of molecular beam etchings of semiconductor surfaces are discussed. The use of time-resolved reflectivity to monitor the in situ etching rate with high spatial and temporal resolution is described, and potential applications of laser-induced fluorescence for identifying reaction products and determining their degree of vibrational excitation are discussed.

### Metal Deposition Using Ultraviolet Photolysis\*

Jacqueline Berg and Peter Yeung TRW, One Space Park Redondo Beach, CA 90278

Deposits containing iron were found following excimer laser photolysis of iron pentacarbonyl. The appearance of the deposits on the surface irradiated by the laser was different if KrF (249nm) was used instead of ArF (193 nm), the latter appearing more metallic. Work is in progress to obtain deposits of other materials.

\*This work was supported by TRW Independent Research and Development funds.

### Amorphization at Low Fluence with Laser Blow-Off Ion Source\*

N. G. Utterback and S. Prussin TRW, One Space Park Redondo Beach, CA 90278

Room temperature silicon single crystal wafers have been driven amorphous by boron ion implants of 2 x  $10^{14}$  B/cm<sup>2</sup> at 25 keV. Annealing these wafers at 550 C for 30 minutes restores the single crystal structure and produces a defect free surface. The ion implanter uses boron ions accelerated from a plasma produced by laser blow-off from a pure boron target. Ion pulses of 10 microseconds at current densities of 1 mA/cm<sup>2</sup> are utilized. An explanation for these results has not been found.

<sup>\*</sup>Supported by Naval Ocean Systems Center, San Diego, CA.

# Integrated Circuit Applications of Laser Deposition and Annealing of Insulator Films

Jere M. Marrs
Applied Research Group
Tektronix, Inc.
Beaverton, OR 97077

The insulator film of most interest in silicon IC technology is SiO<sub>2</sub>. In oxide films other than that thermally grown on Si, the film is deposited by a controlled oxidation of SiH<sub>4</sub>. The control variables are gas pressures, gas composition, and substrate temperature. There are other less well-defined variables such as flow rates and reaction chamber layout. The possibility of a photogenerated SiO<sub>2</sub> film is of great interest because of the anticipated advantages of lower substrate temperatures, additional control variables, higher quality films, and graphic capabilities.

In this presentation, I propose a photochemical system for the deposition of  $SiO_2$  films. The choice and mechanism of the process is discussed. The unique control variables in this system are discussed.

Photothermal treatment of  $\mathrm{Si/SiO_2}$  interfaces (MOS structures) has been shown to reduce surface state densities. As a basis for comparative data, MOS structures have been laser annealed here. The effect of annealing power on surface state densities has been determined and deep-level transient spectroscopy (DLTS) has been utilized to characterize these structures. These data will be presented for comparison with photodeposited  $\mathrm{SiO_2}$  films.

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